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(54) RESIN BLACK MATRIX, BLACK PASTE, COLOR FILTER AND LIQUID CRYSTAL  
DISPLAY ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To make it possible to improve dispersibility, to enhance light shieldability, to improve pattern workability, to obviate film peeling and to improve display grade by dispersing a specific carbon black as a light shielding agent into a resin.

SOLUTION: This black matrix is required to finely disperse the carbon black in order to obtain the high light shieldability and includes the black matrix prepd. by dispersing the specific carbon black as the light shielding material into the resin. The specific carbon black refers to the carbon black satisfying at least one among the following (A) to (D): (A) The pH value is  $\leq 6.5$ . (B) The carboxyl group concn. [COOH] on the surface is  $0.001 < [\text{COOH}]$  in molar ratio per total carbon atom. (C) The hydroxyl group concn. [OH] of the surface is  $0.001 < [\text{OH}]$  in molar ratio per total carbon atom. (D) The sulfone group concn. [SO<sub>3</sub>H] of the surface is  $0.001 < [\text{SO}_3\text{H}]$  in molar ratio per total carbon atom.



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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention][The technical field which carries out invention]. This invention is that for manufacturing the resin black matrix and it which are used for the light filter of a liquid crystal display element, etc.

\*\* which manufactures the resin black matrix and it which are related with a strike, are excellent in a light sheilding in more detail, and have close dimensional accuracy, and have the outstanding characteristic, such as being hard to produce film peeling.

[0002]

[Description of the Prior Art]Generally, the light filter for liquid crystal display comprises many picture elements by making into one picture element the trichromatic pixel of the red formed on the light transmittance state board, green, and blue. And between each pixel, in order to raise display contrast, the shielding region (on the screen, since it generally looks black, called the black matrix) with fixed width is provided.

[0003][0003]. Black MATORITSU \*\*\*\*\* by which the filter was beforehand produced with photolithography method as for the conventional mosquito.

Business is carried out and it is formed with the metal thin film which consists of a detailed pattern.

As metal used for this black matrix, there are Cr, nickel, aluminum, etc. and the vacuum film forming methods, such as a sputtering method and a vacuum deposition method, are widely used as that formation method. Next, in order to form a detailed pattern, after usually forming the pattern of photoresist with photolithography method, a metal thin film is etched by using this resist pattern as an etching mask. By this process, the minute pattern of the metal thin film which is in agreement with the minute pattern of photoresist can be formed.

[0004]How to dye the dyeable medium formed using photolithography method as a method of forming a pixel, There is also the method of forming a coloring portion as a manufacturing method of low cost by print processes and the ink jet method else [, such as a method of using a photosensitive pigment dispersion constituent, the method of etching a nonphotosensitive pigment dispersion constituent, and an electrodeposition process using the patterned electrode, ].

[0005]

[Problem to be solved by the invention]However, the black matrix formed with the metal thin film has a high manufacturing cost in the process of forming a metal thin film, and has become the cause of raising the price of the light filter itself. Since Cr generally used as a metal thin film for black matrices had high reflectance, the reflected light from Cr side was also strong, and when a light filter was especially built into a transmission type display, there was a problem of spoiling display quality remarkably at the strong place of outdoor daylight. In order to make reflectance of a black matrix low, the method of providing a layer like chrome oxide between Cr and a light transmittance state board is proposed, but the manufacturing cost of a black matrix will increase further and is not preferred from a point of a cost cut.

[0006]For this reason, after patterning-izing the resin colored by the shielding agent, for example and forming a black matrix, the method of forming a pixel and manufacturing a light filter is proposed. However, still sufficient light sheilding is not acquired compared with the conventional metal thin film. Therefore, in liquid crystal display, there was a problem that black-matrix \*\* was carried out and a back light leaked to a display surface. Therefore, when a color especially with low black and luminosity was displayed, there was a serious problem that a desired color could not be displayed. On the other hand, although what is necessary is just to thicken thickness of a black matrix in order to raise a light sheilding, the new problem that the surface smoothness on the surface of a light filter falls, and image quality deteriorates shortly occurs.

[0007]this invention was originated in view of many faults of this technology, and the place made into the purpose has a high light sheilding, and is related with the black paste for manufacturing the resin black matrix for light filters and it which can display the image quality which was excellent when it included in a liquid crystal display element.

[0008]

[Means for solving problem]The black paste for manufacturing the following resin black matrices and it can attain the purpose of this this invention.

[0009]Namely, in the resin black matrix which makes it come to distribute a shielding agent in resin, In the resin black matrix using the carbon black which fills at least one of following (A) - (D) as this shielding agent, and the black paste which makes it come to distribute a shielding agent in a resin solution, It is a liquid crystal display element having black paste using the

carbon black which fills at least one of following (A) - (D) as this shielding agent, a light filter having said resin black matrix, and this light filter.

[0010](A) PH value is 6.5 or less.

(B) Surface carboxyl group concentration  $[\text{COOH}]$  is a mole ratio per total carbon atom, and is  $0.001 < [\text{COOH}]$ .

(C) Surface hydroxyl group concentration  $[\text{OH}]$  is a mole ratio per total carbon atom, and is  $0.001 < [\text{OH}]$ .

(D) The sulfone group concentration  $[\text{SO}_3\text{H}]$  of the surface is a mole ratio per total carbon atom, and is  $0.001 < [\text{SO}_3\text{H}]$ .

[0011]

[Mode for carrying out the invention] Hereafter, it explains in detail.

[0012] In order to acquire a high light sheilding, the black matrix of this invention needs to carry out micro-disperse of the carbon black, and distributes carbon black specific as a shielding agent in resin. Specific carbon black is carbon black which fills at least one of following (A) - (D).

[0013](A) PH value is 6.5 or less.

(B) Surface carboxyl group concentration  $[\text{COOH}]$  is a mole ratio per total carbon atom, and is  $0.001 < [\text{COOH}]$ .

(C) Surface hydroxyl group concentration  $[\text{OH}]$  is a mole ratio per total carbon atom, and is  $0.001 < [\text{OH}]$ .

(D) The sulfone group concentration  $[\text{SO}_3\text{H}]$  of the surface is a mole ratio per total carbon atom, and is  $0.001 < [\text{SO}_3\text{H}]$ .

[0014] PH value of carbon black is three or less still more preferably four or less more preferably. If what has PH value of carbon black higher than 6.5 is used, the light sheilding of a black matrix will fall, and also dimensional accuracy worsens, or it becomes easy to produce film peeling, and is not desirable. The pure water 100g is enough mixed with 10 g of carbon black with an ultrasonic wave, and with PH value of carbon black, PH value of the supernatant liquid after cooling is measured with PH meter, a hydrogen-ion density plan, etc. to a room temperature after boiling so that water may not evaporate for 10 minutes.

[0015] As for surface carboxyl group concentration  $[\text{COOH}]$ , it is [ 0.002 or more ] more preferably desirable from a point of a dispersion stability that it is 0.003 or more still more preferably. Although a maximum in particular is not limited,  $[\text{COOH}] = 0.1$  is usually a manufacturing maximum of carbon black.

[0016] As for surface hydroxyl group concentration  $[\text{OH}]$ , it is [ 0.002 or more ] more preferably desirable from a point of a dispersion stability that it is 0.003 or more still more preferably. Although there is a phenolic hydroxyl group in which the alcoholic hydroxyl group in which

neutrality is shown, and acidity are shown as a hydroxyl group, the quantity of a phenolic hydroxyl group is important. Therefore, it is preferred that the concentration of a phenolic hydroxyl group is not less than 50% of the concentration of a hydroxyl group. As for the concentration of a phenolic hydroxyl group, it is preferred that it is 0.005 or more. Although the maximum in particular of surface hydroxyl group concentration  $[\text{OH}]$  is not limited,  $[\text{OH}] = 0.1$  is usually a manufacturing maximum of carbon black.

[0017]As for the sulfone group concentration  $[\text{SO}_3\text{H}]$  of the surface, it is [ 0.002 or more ] more preferably desirable from a point of a dispersion stability that it is 0.003 or more still more preferably. Although a maximum in particular is not limited,  $[\text{SO}_3\text{H}] = 0.1$  is usually a manufacturing maximum of carbon black.

[0018]As a method of changing a fixed quantity of the hydroxyl group concentration on the surface of carbon black, carboxyl group concentration, and sulfone group concentration, the X-ray photoelectron spectroscopy currently called XPS or ESCA can be used. It is effective if X-ray photoelectron spectroscopy is used especially combining a chemical modification method. For example, in order to distinguish a carboxyl group and a hydroxyl group, by making it react to anhydrous trifluoroacetic acid etc. and a hydroxyl group, labeling can be carried out and a fixed quantity of concentration of a hydroxyl group can be changed with F1S peak intensity detected by X-ray photoelectron spectroscopy. By making it react to trifluoroethanol etc. and a carboxyl group, labeling can be carried out and a fixed quantity of concentration of a carboxyl group can be changed with F1S peak intensity detected by X-ray photoelectron spectroscopy.

[0019]On the surface of carbon black, as a method of providing a hydroxyl group and a carboxyl group, With the method, bromine, and water which are oxidized with oxidizers, such as the method of making free oxygen contact and oxidizing under an elevated temperature after manufacturing carbon powder, ozone, and  $\text{NO}_2$ . There are the method of oxidizing with solutions of an oxidizing quality, such as a method, nitric acid, sulfuric acid, etc. which are processed under ordinary pressure or application of pressure, etc., and acidic groups, such as a carboxyl group and a phenolic hydroxyl group, are provided in the powder surface of carbon black. These methods may be combined. Acidic groups, such as a sulfone group, can also be provided by chemical reactions, such as sulfonation by fuming sulfuric acid. By adjusting the grade of these processings, PH value of carbon black is controllable.

[0020]What was manufactured by the contacting method carbon black is called channel black, roller black, and disk black, Although using what was manufactured by thermal \*\* currently called what manufactured by the fur nesting method currently called gas fur nest black and oil fur nest black, thermal black, and acetylene black cuts, Channel black, gas fur nest black, and oil fur nest black are preferred, and especially fur nest black is more preferred.

[0021]In order to raise the light sheilding of a black matrix, it is preferred to use carbon black

with small particle diameter, 5-40 nm has preferred primary [ an average of ] particle diameter, and 6-35 nm is 8-30 nm still more preferably more preferably.

[0022]The structure of carbon black in the inside of a black matrix, If detailed carbon black condenses, the secondary particles of carbon black are formed and the average of this particle diameter is made into secondary [ an average of ] particle diameter, it is preferred to carry out micro-disperse so that secondary [ an average of ] particle diameter may become small, and it is ideal that you do not form secondary particles but make it distribute with sufficient stability by primary particles. As secondary [ an average of ] particle diameter, 5-100 nm is preferred and is 8-75 nm still more preferably 6-88 nm more preferably. If larger than this, sufficient light sheilding is not acquired and it is not desirable. As how to ask for primary [ an average of ] particle diameter and secondary [ an average of ] particle diameter, carbon black is observed, for example with a transmission type or a scanning electron microscope, and it asks for mean particle diameter according to JIS-R6002.

[0023]Carbon black with such small particle diameter mainly has a color tone of a tea system. Therefore, it is preferred to mix the paints of the complementary color to carbon black, and to make it colorless. It is preferred to make it come to distribute the shielding agent which consists of paints of the complementary color to carbon black and this carbon black into resin as a resin black matrix. As the brown complementary color, it is a color of blue or a purple system. As paints for the complementary color, the mixture of a blue pigment or purple paints and also a blue pigment, and purple paints can be used. However, when using colored resin, the paints of the complementary color are used to the mixed colors of resin and carbon black. A color yne DIKUSU (CI) number shows the concrete example of typical paints. Although especially the high organic color of tinting strength is preferred as a blue pigment or purple paints and the pigment blues 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, 21, 22, 60, and 64 etc. are mentioned as an example of a blue pigment, Especially the pigment blues 15, 15:1, 15:2, and 15:6 are preferred. Although the pigment violet 19, 23, 29, 31, 32, 33, 36, 37, 39, 43, and 50 etc. are mentioned as an example of purple paints, especially the pigment violet 23, 31, 33, 43, and 50 is preferred.

[0024]Although various shielding agents may be added as a shielding agent in the range in which a light sheilding is not reduced besides this, in order to acquire a high light sheilding, It is 70 weight % or more still more preferably 60weight % or more preferably [ carrying out the rate of carbon black of closing into a shielding agent to 50weight % or more ], and more preferably. As shielding agents other than carbon black, the mixture of paints, such as red, blue, and green, other than metallic-oxide powder, such as titanium oxide and 4 iron oxide, metallic sulfide powder, and a metal powder, etc. can be used.

[0025]As a colorless resin black matrix of this invention, In a CIE standard colorimetric system, the chromaticity coordinate (x, y) of the transmitted light of a resin black matrix and a reflected

light measured in illuminant C or F10 light source receives the chromaticity coordinate  $(x_0, y_0)$  of this light source,  $(x-x_0)^2+(y-y_0)^2 \leq 0.01$  -- more -- desirable --  $(x-x_0)^2+(y-y_0)^2 < 0.0025$  -- it is  $(x-x_0)^2+(y-y_0)^2 < 0.0004$  still more preferably.

[0026]The back light source for the improvement in visibility is usually provided in the electrochromatic display device. The chromaticity coordinate  $(x, y)$  in the CIE standard colorimetric system of light which leaks through a resin black matrix on a liquid crystal display element at the time of a back light exposure the resin black matrix of this invention, It is preferred that it is  $(x-x_0)^2+(y-y_0)^2 \leq 0.01$  to the chromaticity coordinate  $(x_0, y_0)$  of this back light, more -- desirable --  $(x-x_0)^2+(y-y_0)^2 < 0.0025$  -- it is  $(x-x_0)^2+(y-y_0)^2 < 0.0004$  still more preferably.

[0027]As for the back light, the red of a light filter, blue, and the three-wave light source that energy concentrates on the peak of the transmission spectrum of a green picture element are usually used. In three specific waves, a three-wave light source has a strong peak of luminous energy in a visible range (400-700 nm), and calls this dominant wavelength. As a definition of dominant wavelength, focusing on the highest peak of the luminous energy of the blue series color in the range of 400-490-nm wavelength, the range of  $\pm 10$  nm, With the greenish color in the range of 490-580-nm wavelength, it is considered [ center / peak / most energy-rich ] as the range of  $\pm 10$  nm a center [ the most energy-rich peak ] in the light of the reddish color in the range of  $\pm 10$  nm, and the range of 580-675-nm wavelength. Usually, it is the range of 440-460 nm, 530-550 nm, and 600-620 nm.

[0028]As transmissivity of a resin black matrix in each of such dominant wavelength, it is preferred that those maximums do not exceed 4 times of the minimum, and it is preferred not to exceed twice more preferably and not to exceed 1.5 times still more preferably. If a difference becomes large more, light which has leaked through a three-wave light source will color, and at least an image display article will be spoiled. However, as transmissivity of a resin black matrix in each dominant wavelength, it is considered as average value in three  $\pm 10$  nm- $\pm 10$  nm points a center [ the most energy-rich peak ].

[0029]As for a black matrix, it is preferred that optical density per 1 micrometer of thickness of a black matrix has 2.3 or more light shieldings in a light region with a wavelength of 430-640 nm. It is 3.5 or more still more preferably 3.1 or more more preferably. Hereafter, in a light region with a wavelength of 430-640 nm, optical density per 1 micrometer of thickness is defined as a light shielding. In order to raise a light shielding, it is important to raise distribution and a dispersion stability of a shielding agent. In order to acquire such a high light shielding, it is desirable to make more preferably into 60 weight % or more still more preferably a rate of carbon black contained in a black matrix 45weight % or more 35weight % or more.



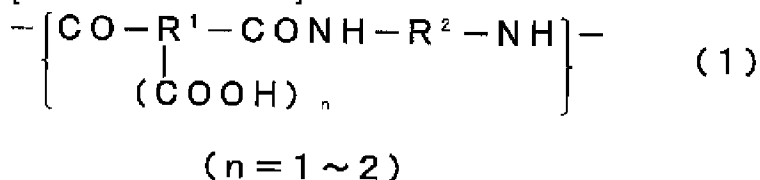
[0030]As for the reference stimuli Y in the CIE standard colorimetric system of the black matrix in a light region with a wavelength of 400-700 nm, it is preferred that it is 0.50 or less, and they are 0.025 or less still more preferably 0.079 or less more preferably.

[0031]0.75 micrometer or less is 0.5 micrometer or less still more preferably preferably [ using less than 1 micrometer ] as thickness of a black matrix, and more preferably. The \*\*\*\*\* difference in a light filter becomes small, and is so preferred that thickness of a black matrix is made thin. By the thickness of a black matrix being 0.5 micrometer or less, a protective layer can also be omitted and it is especially desirable. Although not limited especially as a minimum, 0.3 micrometers or more are preferred from points, such as intensity of a black matrix, and dimensional accuracy of a pattern.

[0032]As resin for black matrices, polyimide resin, an acrylic resin, PVA, gelatin, polyester resin, polyvinyl resin, etc. are mentioned. It is preferred to have heat resistance higher than the resin used for a pixel or a protective film, and the polyimide resin which has the heat resistance of not less than 250 \*\* is more preferred. Although polyamidoimide is also contained and it is not limited in particular as polyimide resin, what imide-izes the polyimide precursor (n= 1-2) which uses as the main ingredients the structural unit usually expressed with a general formula (1) according to heating or a suitable catalyst is used suitably.

[0033]

[Chemical formula 1]



R<sup>1</sup> is a trivalent or tetravalent organic group which has at least two or more carbon atoms among the above-mentioned general formula (1). From a heat-resistant field, R<sup>1</sup> contains cyclic hydrocarbon, an aromatic ring, or an aromatic heterocycle, and its trivalent or tetravalent basis of the carbon numbers 6-30 is preferred. As an example of R<sup>1</sup>, a phenyl group, a biphenyl group, a terphenyl group, Although a naphthalene group, a perylene group, a diphenyl ether group, a diphenylsulfone group, a diphenylpropane group, a benzophenone group, a biphenyl trifluoropropane group, a cyclobutyl group, a cyclopentyl group, etc. are mentioned, it is not limited to these.

[0034]Although R<sup>2</sup> is a divalent organic group which has at least two or more carbon atoms, from a heat-resistant field, R<sup>2</sup> contains cyclic hydrocarbon, an aromatic ring, or an aromatic heterocycle, and its divalent basis of the carbon numbers 6-30 is preferred.

[0035]As an example of R<sup>2</sup>, a phenyl group, a biphenyl group, a terphenyl group, Although a

naphthalene group, a perylene group, a diphenyl ether group, a diphenylsulfone group, a diphenylpropane group, a benzophenone group, a biphenyl trifluoropropane group, a diphenylmethane group, a dicyclohexyl methane group, etc. are mentioned, it is not limited to these.

[0036]\*\*\*\*\* of the polymer which uses a structural unit (1) as the main ingredients is also good at the copolymer which  $R^1$  and  $R^2$  may comprise one sort respectively among these, and comprises two or more sorts respectively. In order to raise an adhesive property with a substrate, it is preferred to carry out copolymerization of the bis(3-aminopropyl)tetramethyl disiloxane which has siloxane structure as a diamine component in the range in which heat resistance is not reduced.

[0037]As a concrete example of the polymer used as the main ingredients, a structural unit (1) Pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 3,3',4,4'-biphenyl TORIFURUFORO propane tetracarboxylic dianhydride, One or more sorts of carboxylic acid dianhydride chosen from the group which consists of 3,3',4,4'-biphenyl sulfone tetracarboxylic dianhydride, 2,3,5, - bird carboxy cyclopentylacetic acid dianhydride, etc., A p phenylenediamine, 3,3'-diaminodiphenyl ether, 4-4'-diaminodiphenylether, 3, 4'-diaminodiphenyl ether, Although the polyimide precursor compounded from one or more sorts of diamine chosen from groups, such as 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminohexylmethane, and 4,4'-diamino JIFENI methane, is mentioned, It is not limited to these. These polyimide precursors combine selectively a publicly known method, i.e., tetracarboxylic dianhydride and diamine, and are compounded by making it react in a solvent.

[0038]The molecular terminal of a polyimide precursor is closed, and in order to suspend a polymerization, dicarboxylic anhydrides, such as a maleic anhydride, are usually added. However, the dispersibility of the direction whose molecular terminal of polyimide resin is an amine group of a shielding agent improves, and it is still more preferred. The percentage that a molecular terminal is an amine group is not less than 90% still more preferably not less than 80% more preferably not less than 50%. In order to make the molecular terminal of polyimide resin into an amine group, it is preferred at the time of composition of a polyimide precursor to make it react in a solvent, as the number of mols of diamine is made a little large to the number of mols of tetracarboxylic dianhydride. Specifically, 100-90 mol of tetracarboxylic dianhydride [ 98-93 mol of ] shall be 97-95 mol still more preferably more preferably to 100 mol of diamine.

[0039]Also in these polyimide resin, the direction of the high thing of the optical absorption in the wavelength of a light region becomes high, and the light sheilding of a black matrix also has it. [ especially more preferred ] That is, in the polyimide film of 2 micrometers of thickness, it is 80 or less still more preferably 90 or less preferably [ that the reference stimuli Y in the CIE

standard colorimetric system in visible light with a wavelength of 400-700 nm use 96 or less polyimide resin ], and more preferably.

[0040]Specifically, for example as tetracarboxylic dianhydride, It is so desirable that the electronic suction nature of an acid dianhydride residue is high, and the ketone type thing like a benzophenone group, the ether type thing like a diphenyl ether group, the thing that has a phenyl group, the thing which has a sulfone group like a diphenylsulfone group, etc. are preferred. For example, it is pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 3,3', and 4,4'-biphenyl tetracarboxylic acid 2 anhydride etc. It is so desirable that electron-donative [ of diamine residue ] is strong as diamine, and A biphenyl group, What has p-, p-substitution or m-, diaminodiphenyl ether of p-substitution structure, methylenedianiline, a naphthalene group, a perylene group, etc. is preferred, and is 4, 4' or 3, 4'diaminodiphenyl ether, a p phenylenediamine, etc. It is also preferred to have the structure where the nitro group was replaced by these aromatic rings.

[0041]The resin black matrix of this invention can be made to form by the applying method using the black paste which distributed the shielding agent which consists of said specific carbon black into a resin solution.

[0042]As how to ask for the primary [ an average of ] particle diameter of carbon black in black paste, and secondary [ an average of ] particle diameter, carbon black is observed, for example for black paste with a transmission type or a scanning electron microscope after spreading and desiccation, and it asks for mean particle diameter according to JIS-R6002.

[0043]It is preferred to mix the paints of the complementary color to carbon black, and to make it colorless, and it is preferred to make it come to distribute the shielding agent which consists of paints of the complementary color to carbon black and this carbon black into a resin solution as black paste of this invention. For example, the mixture of a blue pigment or purple paints and also a blue pigment, and purple paints can be used, and the high organic color of tinting strength is preferred especially.

[0044]Although various shielding agents may be added as a shielding agent in the range in which a light sheilding is not reduced besides this, in order to acquire a high light sheilding, It is 70 weight % or more still more preferably 60weight % or more preferably [ carrying out the rate of carbon black of closing into a shielding agent to 50weight % or more ], and more preferably. As shielding agents other than carbon black, the mixture of paints, such as red, blue, and green, other than metallic-oxide powder, such as titanium oxide and 4 iron oxide, metallic sulfide powder, and a metal powder, etc. can be used.

[0045]As a color of the transmitted light of the black paste of this invention, In the conditions from which the reference stimuli Y are set to  $0.03 \leq Y \leq 0.3$  in a CIE standard colorimetric system using illuminant C or F10 light source, A chromaticity coordinate (x, y) receives the chromaticity coordinate  $(x_0, y_0)$  of a light source,  $(x-x_0)^2 + (y-y_0)^2 \leq 0.01$  it is preferred that it is

-- more -- desirable --  $(x-x_0)^2 + (y-y_0)^2 < 0.0025$  -- it is  $(x-x_0)^2 + (y-y_0)^2 < 0.0004$  still more preferably.

[0046]As the color measurement method of the transmitted light of black paste, light transmission is measured first. Specified quantity spreading of the black paste is carried out on glass, and there are a method of measuring transmissivity with a spectrophotometer, the method of putting black paste into a glass cell and measuring transmissivity with a spectrophotometer, etc. From beam-of-light penetration SUPEKURU, the reference stimuli X, Y, and Z in illuminant C or F10 light source are calculated, and a chromaticity coordinate is calculated.

[0047]As a resin solution, solutions, such as a polyimide precursor, an acrylic resin, PVA, gelatin, polyester resin, and polyvinyl resin, can be used. It is preferred to have heat resistance higher than the resin used for a pixel or a protective film, and the polyimide precursor solution which has the heat resistance of not less than 250 °C is preferred. As a polyimide precursor, said polyimide precursor can be used preferably.

[0048]Therefore, also in a polyimide precursor, the direction of the high thing of the optical absorption in the wavelength of a light region becomes high, and the light shielding of a black matrix also has it. [ especially more preferred ] That is, in the polyimide film of 2 micrometers of thickness, it is 80 or less still more preferably 90 or less preferably [ that the reference stimuli Y in a CIE standard colorimetric system use 96 or less polyimide resin ], and more preferably. These values are calculable by measuring the light transmission spectrum of the polyimide film in visible light with a wavelength of 400-700 nm. Specifically, for example as tetracarboxylic dianhydride, It is so desirable that the electronic suction nature of an acid dianhydride residue is high, and the ketone type thing like a benzophenone group, the ether type thing like a diphenyl ether group, the thing that has a phenyl group, the thing which has a sulfone group like a diphenylsulfone group, etc. are preferred. For example, it is pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 3,3', and 4,4'-biphenyl tetracarboxylic acid 2 anhydride etc. It is so desirable that electron-donative [ of diamine residue ] is strong as diamine, and A biphenyl group, What has p-, p-substitution or m-, diaminodiphenyl ether of p-substitution structure, methylenedianiline, a naphthalene group, a perylene group, etc. is preferred, and is 4, 4' or 3, 4'diaminodiphenyl ether, a p phenylenediamine, etc. It is also preferred to have the structure where the nitro group was replaced by these aromatic rings.

[0049]As a black paste solvent, although amide system polar solvents, such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, and N,N-dimethylformamide, a lactone system polar solvent, dimethyl sulfoxide, etc. are used suitably, usually, In order to heighten the dispersion effect of carbon black, what contains an amide system polar solvent at least is preferred, and it is preferred that an amide system polar solvent uses more preferably the solvent which consists of the main ingredients or an amide system polar-solvent independent. In the case of

the mixed solvent which consists of a solvent of  $n$  kind, the solvent whose amide system polar solvent is the main ingredients here means containing more mostly than  $x(1/n)$  100 weight %. For example, in the case of the solvent of the two-component system, it says that more amide system polar solvents than 50 weight % contain, and, in the case of the solvent of three component systems, says that many amide system polar solvents contain from 33 weight %.

[0050]When also adding shielding agents other than carbon black, in order to heighten the dispersion effect of a shielding agent, it is preferred that a lactone system polar solvent is included further at least. When rosin resin acid is especially used as a dispersing agent, it acts effectively especially. Although lactone says the compound of the carbon numbers 3-12 by aliphatic series cyclic ester and beta propiolactone, gamma-butyrolactone, gamma-valerolactone, delta-valerolactone, gamma-caprolactone, epsilon-caprolactone, etc. are mentioned as a concrete example, In respect of the solubility of especially a polyimide precursor, gamma-butyrolactone is preferred. For this reason, it is more preferred to use the mixed solvent of an amide system polar solvent and a lactone system polar solvent.

[0051]For the reason on a spreading disposition, as solvents other than these Methyl cellosolve, The quicker solvent of vapor rates, such as ethylcellosolve, methylcarbitol, ethylcarbitol, and ethyllactate, It is preferably [ it is preferred to add the ether acetate solvent of ethylene glycol or propylene glycol whose surface tension is 26-33 dynes/cm, and ] desirable among all the solvents to make it mix five to 20weight % still more preferably one to 25weight %. Specifically, there are propylene-glycol-methyl-ether acetate, 3-methyl-3-methoxy butyl acetate, ethylene glycol ethyl ether acetate, 3-methoxy butyl acetate, etc. In the direction which distributes shielding agents, such as carbon black, in the solution which added these solvents, generation of heat at the time of distribution becomes small, and gelling becomes being hard to produce, or dispersibility improves, and it is more desirable.

[0052]Methods of distributing shielding agents, such as carbon black, include the method of distributing in dispersion machines, such as 3 rolls, a Sand grinder, and a ball mill, etc., for example, after mixing a shielding agent and a dispersing agent in a resin solution. When also using shielding agents other than carbon black, after distributing each shielding agent independently, respectively, the method of preparing after distribution, etc. are more suitably used, respectively by dividing the method of mixing these, or carbon black and the other shielding agent. For [ when using a polyimide precursor as resin ] prevention, such as a viscosity rise by the reaction between the polyimide precursors under distribution, and the reaction of a shielding agent and a polyimide precursor, and gelling, After mixing a shielding agent in a solvent first and making pre dispersion perform, the method of mixing or distributing a polyimide precursor later is more preferred. The method of distributing or mixing with the solvent which fitted distribution in shielding agents other than carbon black or carbon black, respectively, or the polyimide precursor containing the solvent is more preferred. As for

distributed intensity, dispersion time, etc., adjusting suitably is preferred in order to carry out micro-disperse of the shielding agent.

[0053] It is preferred that a yield value by a flow equation of Casson is 0.1 Pa or less as a rheology characteristic of black paste, and it is 0.001 Pa or less still more preferably 0.01 Pa or less more preferably. Since a yield value will become large, an aggregation of a shielding agent will take place and the light shielding of a black matrix will fall rather than this if the dispersion stability of a shielding agent is bad, it is not desirable. In order to use predetermined carbon black for black paste of this invention, a low yield value is acquired. If it is  $S$  = shearing stress,  $D$  = shear rate, a  $\tau_0$  = yield value, and  $\mu_0$  = Casson viscosity, a flow equation will be expressed with the equation 1 and a yield value will be calculated by a square of a section of  $S^{1/2}$  axis in a graph of  $S^{1/2}$  to  $D^{1/2}$ .

[0054]

[Mathematical formula 1]

$$\sqrt{S} = \sqrt{\tau_0} + \sqrt{\mu_0} \cdot \sqrt{D} \quad (\text{式 1})$$

Although viscosity is suitably prepared in accordance with a coating method, its 5 - 1000cP is preferred, and it is 10 - 100cP still more preferably eight to 150 cP more preferably.

[0055] Various additive agents can be added to black paste for the purpose of improvement in dispersibility of a shielding agent. Besides this, various additive agents, a surface-active agent, etc. can be added for the purpose of a spreading nature and leveling disposition top.

[0056] Next, on a light transmittance state board, the light filter for liquid crystal display elements which makes this order come to laminate a resin black matrix, a pixel, and a protective film is made into an example, and is explained. First, black paste is applied on a light transmittance state board. Especially as a light transmittance state board, it is not limited and a film or a sheet of inorganic glass, such as silica glass, borosilicate glass, and soda lime glass that carried out silica coating of the surface, and organic plastics, etc. is used preferably. As for a coating method, spin coating methods other than dip spreading and a roll coater, such as HOERA and a spinner, are used for a good target. Then, it dries with hot wind oven, a hot plate, etc., and a semi cure is carried out. Although semi cure conditions change a little with the kinds and coverage of the used polyimide precursor, it is common to usually heat at 100-180 °C for 1 to 60 minutes. When a nonphotosensitive polyimide precursor is used, photoresist is applied and prebaked after this and it exposes using an optical mask. Then, the development of a resist and patternizing of a black matrix are continuously performed with dip, a shower, a paddle method, etc. using a developing solution. Then, a resist is exfoliated with dip, a shower, a paddle method, etc. using release liquid. Finally, in order to imide-ize, at 200-400 °C, it heats for 1 to 60 minutes, and a cure is carried out. Between black matrices, an about 20-200-micrometer opening is usually provided, and a pixel is formed in this space by a post

process.

[0057]Next, the pixel of a plural color is formed in the opening of a black matrix. Usually, the colors of the pixel of each pixel are red and three blue and green colors, and are colored by colorant. As colorant used for a pixel, an organic color, an inorganic pigment, a color, etc. can be used conveniently. As an organic color, a phthalocyanine system, a horse mackerel rake system, condensation azo, a quinacridone series, an anthraquinone system, a perylene system, a peri non system, etc. are used suitably. As resin used for a pixel, epoxy system resin, acrylic, It is preferred to be able to use the material of photosensitivity or nonphotosensitivity, such as animal protein resin in which dyeing, such as polyimide system resin, urethane system resin, polyester system resin, polyvinyl system resin, and gelatin, is possible, to make it distribute or dissolve and to color colorant into these resin.

[0058]First, the resin paste containing colorant is applied. Spin coating methods other than dip spreading and a roll coater, such as HOERA and a spinner, are used suitably. then, the thing to dry with a hot wind, a hot plate, etc. -- the coloring layer of the 1st amorous glance is formed over the whole surface on a black matrix. Usually, since a light filter consists of a pixel of a plural color, it removes an unnecessary portion with photolithography method, and forms the pixel pattern of the 1st desired amorous glance. As pixel thickness, it is about 0.5-3 micrometers. Only the pixel of a required color repeats this, the pixel which consists of two or more colors is formed, and a light filter is manufactured.

[0059]Then, a protective film is laminated if needed. As a protective film, there are an acrylic resin, an epoxy resin, silicone resin, polyimide resin, etc., and it is not limited in particular.

[0060]After forming a pixel beforehand patternized on a light transmittance state board besides this, photosensitive black paste is applied, it exposes from the light transmittance state board side, and there are a method of forming a black matrix between pixels, using a pixel as a mask, what is called a back-side-exposure system, etc.

[0061]Finally, lamination of an ITO transparent electrode, patterning, etc. can be performed by a general method if needed.

[0062]It provides in the substrate side which counters also besides providing in the light filter side of a liquid crystal display element as mentioned above, and a resin black matrix for liquid crystal display elements of this invention is \*\*\*\*. For example, in TFT-LCD, it may provide in the stripe like electrode board side with which the TFT matrix array board side is countered in MIM-LCD, and the MIM matrix array board side is countered in STN-LCD.

[0063]Thus, in order to manufacture a liquid crystal display element in which a light filter which has the manufactured resin black matrix was carried, it can be based, for example on the following methods. A liquid crystal orientation film is first formed on a light filter, and rubbing treatment is performed. An orienting film is formed similarly and it combines with a counter substrate which performed rubbing treatment. Subsequently, an electrochromatic display

display device which has the above-mentioned light filter inside a liquid crystal cell is obtained by pouring in a liquid crystal between substrates and assembling a liquid crystal cell.

[0064]A liquid crystal display element of this invention is compared with a liquid crystal display element which has the conventional black matrix, Reflectance of the black matrix is mainly low, Outstanding display properties that there is no tint of (5) reflections with a small reflect lump of (4) backgrounds with (3) black appropriate for [ backgrounds ] black which originates in a colorless thing and where (1) (2) red and green and blue coloring to which contrast of a display does not fall look skillfully also at a bright place are shown.

[0065]Hereafter, although an working example explains this invention concretely, this invention is not limited to these.

[0066]

[Working example]

[manufacture of a polyimide precursor solution] -- 3,3',4,4'-biphenyl tetracarboxylic dianhydride [ ] -- 147 g -- N-methyl-2-pyrrolidone [ ] -- with 775 g, [ teach and ] 4-4'-diaminodiphenylether 95.10g and bis(3-aminopropyl)tetramethyl disiloxane Added 6.20 g, it was made to react at 60 \*\* for 3 hours, and a polyimide precursor solution with a viscosity of 600 P (25 \*\*) was obtained. An average degree of polymerization is about 27, and both ends had an amine group. 120 \*\* after applying and carrying out hot air drying of this for 80 \*\* 10 minutes so that it may be finished in a spinner on an alkali-free-glass (product [ made from NEC Glass ], "OA-2") board and thickness may be set to 2 micrometers -- a semi cure during 20 minutes -- the cure was carried out for 300 \*\* 30 minutes. The reference stimuli Y of this polyimide film were 95.

[0067]The whole quantity was mixed for the carbon black mill base and blue paints mill base which have the presentation of the working-example 1 following after distribution for 30 minutes at 7000 rpm using the homogenizer, respectively, \*\*\*\* removed the glass bead, and black paste was prepared. The viscosity of black paste is 30cP.

The yield value was  $2.0 \times 10^{-4}$  Pa.

As a shielding agent, the blue pigment was used as brown carbon black and its complementary color pigment.

[0068]

(1) Carbon black mill base carbon black (the PH value 2.8 and the primary [ an average of ] particle diameter of 28 nm) The secondary [ an average of ] particle diameter of 55 nm, 4.6 copies of fur nest blacks Polyimide precursor solution . N-Methyl-Pyrrolidone 61.4 Copy Copies [ 23.0 ] . Glass bead 90.0-copy (2) blue paints mill base . BIGUMENTO blue 15 gamma-butyrolactone 63.6-copy glass bead 90.0-copy alkali free glass 2.2 copies (the product made from NEC Glass.) 0.2 copy of polyimide precursor solution 23.0-copy Abieticacid On the "OA-2" board, by the spinner, spreading and after carrying out hot air drying for 80 \*\* 10 minutes, the semi-cure was carried out for 20 minutes at 120 \*\*. Then, 80 \*\* of positives resist



(Shipley "Microposit" RC100 30cp) were dried after spreading by the spinner for 20 minutes. It exposes via a photo mask using product exposure machine PLA[ made from Canon ]-501F, After the alkali developing solution (Shipley "Microposit" 351) performed simultaneously development of a positive resist, and etching of the polyimide precursor, the positive resist was exfoliated of methyl Cellosolve acetate. The cure was carried out for 300 °C 30 minutes. Thus, the opening established the lattice-like black matrix which are 240 micrometers of lengthwise directions, and 60 micrometers of transverse directions at 0.98 micrometer in thickness.

[0069]Next, red, the JIAN truck quinone system paints respectively shown by ColorIndex No.65300 Pigment Red 177 as green and blue paints, The copper-phthalocyanine-blue system paints shown by Phthalocyanine Green system paints Color Index No.74160 Pigment Blue 15-4 shown by Color Index No.74265 Pigment Green 36 were prepared. Mixture dispersion of the above-mentioned paints was respectively carried out to the polyimide precursor solution, and red and three kinds of green and blue coloring pastes were obtained. First, hot air drying of the green paste was applied and carried out to the black-matrix forming face side of the glass substrate of a light transmittance state for 80 °C 10 minutes, and the semi-cure was carried out for 20 minutes at 120 °C. Then, 80 °C of positives resist (Shipley "Microposit" RC100 30cp) were dried after spreading by the spinner for 20 minutes. After it exposes using a mask and an alkali developing solution (Shipley "Microposit" 351) performs simultaneously development of a positive resist, and etching of a polyimide precursor, The positive resist was exfoliated of methyl Cellosolve acetate, and the green picture element of stripe shape was set crosswise to pitch 300micrometer at about 90 micrometers in width at the lengthwise direction. The cure was carried out for 300 °C 30 minutes. The thickness of the picture element layer was 1.5 micrometers. After rinsing, similarly, the red of stripe shape and a blue pixel were formed so that the pixel interval of three colors might be set to 10 micrometers.

[0070]Next, a protective film was laminated. As a protective film, acetic acid was added to methyl trimetoxysilane, it hydrolyzed into it, and an organosilane condensate was obtained. A condensate which is mixed, makes 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3-aminopropyl triethoxysilane react at a rate of 1:2 by a mole ratio in a N-methyl-2-pyrrolidone solvent, and has an imido group was obtained. A constituent which mixed this organosilane mixture, a condensate which has this imido group, and N-methyl-2-pyrrolidone at a rate of 5:2:4 by a weight ratio, Spreading and a protective layer with a thickness of 3.0 micrometers which carries out a cure and consists of a polyimide denaturation silicone polymer were obtained on a base substance in which red and an organic blue and green coloring layer were formed.

[0071]The light sheilding of a black matrix did not almost have wavelength dependency, and were 2.5-2.8 (optical density /μm) in wavelength of 430-640 nm. The reference-stimuli value Y in wavelength of 400-700 nm at this time was 0.40.

[0072]The whole quantity was mixed for a carbon black mill base which has the presentation of the working-example 2 following, a purple paints mill base, and a blue paints mill base after distribution for 30 minutes at 7000 rpm using a homogenizer, respectively, a glass bead was \*\*\*\*(ed) and removed, and black paste was prepared. Viscosity of black paste is 33cP.

A yield value was  $1.0 \times 10^{-4}$  Pa.

As a shielding agent, a blue pigment and purple paints were used as brown carbon black and its complementary color pigment.

[0073]

(1) Carbon black mill base carbon black (the PH value 3.5 and primary [ an average of ] particle diameter of 32 nm) Secondary [ an average of ] particle diameter of 60 nm, 2.3 copies of fur nest blacks Polyimide precursor solution . N-Methyl-Pyrrolidone 61.2 Copy Copies [ 8.0 ] . Glass bead 71.5-copy (2) purple paints mill base . Pigment violet 23 0.3 copy A polyimide precursor solution 1.2 copies Gamma-butyrolactone 2.2 copies A glass bead 3.7-copy (3) blue paints mill base BIGUMENTO blue 15 1.1 copy Abieticacid. copy [ 0.1 ] a polyimide precursor solution [ ] -- 4.9 copies gamma-butyrolactone [ ] -- 8.8 copies A light filter was obtained like less than the glass bead 14.9 copy and an working example 1. However, thickness of a black matrix could be 0.75 micrometer. The light sheilding of a black matrix did not almost have wavelength dependency, and were 3.1-3.4 (optical density /mum) in wavelength of 430-640 nm. The reference-stimuli value Y in wavelength of 400-700 nm at this time was 0.32.

[0074]The whole quantity was mixed for the carbon black mill base which has the presentation of the working-example 3 following, the purple paints mill base, and the blue paints mill base after distribution for 30 minutes at 7000 rpm using the homogenizer, respectively, the glass bead was \*\*\*\*(ed) and removed, and black paste was prepared. The viscosity of black paste is 25cP.

The yield value was  $4.7 \times 10^{-4}$  Pa.

As a shielding agent, a blue pigment and purple paints were used as brown carbon black and its complementary color pigment.

[0075]

(1) Carbon black mill base carbon black (the PH value 6.0 and the primary [ an average of ] particle diameter of 26 nm) The secondary [ an average of ] particle diameter of 55 nm, 2.3 copies of fur nest blacks Polyimide precursor solution . N-Methyl-Pyrrolidone 61.2 Copy Copies [ 6.6 ] . Glass bead 71.5-copy (2) purple paints mill base . Pigment violet 23 0.3 copy Polyimide precursor solution 1.0 copy Gamma-butyrolactone 2.2 copies Glass bead 3.7-copy (3) blue paints mill base BIGUMENTO blue 15 1.1 copy Abieticacid. copy [ 0.1 ] polyimide precursor solution [ ] -- 4.0 copies gamma-butyrolactone [ ] -- 8.8 copies The light filter was obtained like less than the glass bead 14.9 copy and the working example 1. However, the

thickness of the black matrix could be 0.66 micrometer. The light shielding of a black matrix did not almost have wavelength dependency, and were 3.5-3.8 (optical density / $\mu\text{m}$ ) in the wavelength of 430-640 nm. The reference-stimuli value Y in the wavelength of 400-700 nm at this time was 0.33.

[0076]A light filter was obtained like working-example 4 working example 3. However, thickness of a black matrix could be 0.95 micrometer. The light shielding of a black matrix did not almost have wavelength dependency, and were 3.5-3.8 (optical density / $\mu\text{m}$ ) in wavelength of 430-640 nm. The reference-stimuli value Y in wavelength of 400-700 nm at this time was 0.025.

[0077]The whole quantity was mixed for a carbon black mill base and a blue paints mill base which have the presentation of the working-example 5 following after distribution for 30 minutes at 7000 rpm using a homogenizer, respectively, \*\*\*\* removed a glass bead, and black paste was prepared. Viscosity of black paste is 32cP.

A yield value was  $1.0 \times 10^{-4}$  Pa.

As a shielding agent, a blue pigment was used as brown carbon black and its complementary color pigment.

[0078]

(1) Carbon black mill base carbon black ([COOH] =0.004 and primary [ an average of ] particle diameter of 26 nm) Secondary [ an average of ] particle diameter of 57 nm, 4.6 copies of fur nest blacks Polyimide precursor solution . N-Methyl-Pyrrolidone 61.4 Copy Copies [ 23.0 ] . A glass bead 90.0-copy (2) blue paints mill base BIGUMENTO blue 15 2.2 copies 0.2 copy of polyimide precursor solution 23.0-copy Abieticacid Gamma-butyrolactone 63.6 copies A glass bead 90.0 or less copies, A light filter was obtained like an working example 1. The light shielding of a black matrix did not almost have wavelength dependency, and were 2.5-2.8 (optical density / $\mu\text{m}$ ) in wavelength of 430-640 nm. The reference-stimuli value Y in wavelength of 400-700 nm at this time was 0.40.

[0079]The whole quantity was mixed for the carbon black mill base which has the presentation of the working-example 6 following, the purple paints mill base, and the blue paints mill base after distribution for 30 minutes at 7000 rpm using the homogenizer, respectively, the glass bead was \*\*\*\*(ed) and removed, and black paste was prepared. The viscosity of black paste is 25cP.

The yield value was  $5.0 \times 10^{-5}$  Pa.

As a shielding agent, a blue pigment and purple paints were used as brown carbon black and its complementary color pigment.

[0080]

(1) Carbon black mill base carbon black ([OH] =0.005 and the primary [ an average of ] particle diameter of 30 nm) The secondary [ an average of ] particle diameter of 60 nm, 2.3 copies of

fur nest blacks Polyimide precursor solution . N-Methyl-Pyrrolidone 61.2 Copy Copies [ 8.0 ] . Glass bead 71.5-copy (2) purple paints mill base . Pigment violet 23 0.3 copy Polyimide precursor solution 1.2 copies Gamma-butyrolactone 2.2 copies Glass bead 3.7-copy (3) blue paints mill base BIGUMENTO blue 15 1.1 copy Abieticacid. copy [ 0.1 ] polyimide precursor solution [ ] -- 4.9 copies gamma-butyrolactone [ ] -- 8.8 copies The light filter was obtained like less than the glass bead 14.9 copy and the working example 1. However, the thickness of the black matrix could be 0.75 micrometer. The light sheilding of a black matrix did not almost have wavelength dependency, and were 3.1-3.4 (optical density /mum) in the wavelength of 430-640 nm. The reference-stimuli value Y in the wavelength of 400-700 nm at this time was 0.32.

[0081] It changed into the carbon black mill base presentation which has the presentation of the working-example 7 following, and also black paste was prepared like the working example 6. The viscosity of black paste is 27cP.

The yield value was  $7.0 \times 10^{-4}$  Pa.

[0082]

(1) Carbon black mill base carbon black ( $[\text{SO}_3\text{H}] = 0.005$  and the primary [ an average of ] particle diameter of 25 nm) The secondary [ an average of ] particle diameter of 55 nm, and 2.3 copies of fur nest blacks Polyimide precursor solution 8.0-copy N-methyl pyrrolidone 61.2 copies Glass bead The light filter was obtained like 71.5 or less copies and the working example 1. The light sheilding of a black matrix did not almost have wavelength dependency, and were 3.1-3.4 (optical density /mum) in the wavelength of 430-640 nm. The reference-stimuli value Y in the wavelength of 400-700 nm at this time was 0.32.

[0083] The light filter was obtained like the working example 1 except having used the following for comparative example 1 carbon black.

[0084]

The viscosity of 4.6 copies of carbon black (PH value 8.0, primary [ an average of ] particle diameter [ of 30 nm ], secondary [ an average of ] particle diameter [ of 80 nm ], fur nest black) black paste is 55cP.

The yield value was 0.25 Pa.

Compared with the working example 1, in the wavelength of 430-640 nm, 1.9-2.3 (optical density /mum), and wavelength dependency increased, and the light sheilding also fell, and the light sheilding of the black matrix was a rejection. The reference-stimuli value Y in the wavelength of 400-700 nm at this time was 0.70.

[0085]The whole quantity was mixed for the carbon black mill base which has the presentation of the comparative example 2 following after distribution for 30 minutes at 7000 rpm using the homogenizer, respectively, \*\*\*\* removed the glass bead, and black paste was prepared. The

viscosity of black paste is 55cP.

The yield value was 0.2 Pa.

Only brown carbon black was used as a shielding agent.

[0086]

(1) Carbon black mill base carbon black (the PH value 8.0 and the primary [ an average of ] particle diameter of 30 nm) The secondary [ an average of ] particle diameter of 80 nm, and 4.6 copies of fur nest blacks Polyimide precursor solution 57.0-copy N-methyl pyrrolidone 120.0 copies The light filter was obtained like the glass bead 180.0-copy working example 1. However, the thickness of the black matrix could be 1.4 micrometers. The light sheilding of the black matrix had strong wavelength dependency, and the light sheilding fell by the long wavelength side. Light sheildings were 1.5-2.2 (optical density /mum), and a rejection in the wavelength of 430-640 nm. The reference-stimuli value Y in the wavelength of 400-700 nm at this time was 0.3.

[0087]The light filter was obtained like the working example 1 except having used the following for comparative example 3 carbon black.

[0088]

The viscosity of 4.6 copies of carbon black ([COOH] <=0.001, [OH] <=0.001, [SO<sub>3</sub>H] <=0.001, primary [ an average of ] particle diameter [ of 55 nm ], secondary [ an average of ] particle diameter [ of 110 nm ], fur nest black) black paste is 60cP.

The yield value was 0.30 Pa.

Compared with the working example 1, in the wavelength of 430-640 nm, 1.9-2.3 (optical density /mum), and a light sheilding fell, and the light sheilding of the black matrix was a rejection. The reference-stimuli value Y in the wavelength of 400-700 nm at this time was 0.80.

[0089]The whole quantity was mixed for the carbon black mill base which has the presentation of the comparative example 4 following after distribution for 30 minutes at 7000 rpm using the homogenizer, respectively, \*\*\*\* removed the glass bead, and black paste was prepared. The viscosity of black paste is 55cP.

The yield value was 0.2 Pa.

Only brown carbon black was used as a shielding agent.

[0090]

(1) Carbon black mill base carbon black ([COOH] <=0.001, [OH] <=0.001, [SO<sub>3</sub>H] <=0.001, and the primary [ an average of ] particle diameter of 55 nm) The secondary [ an average of ] particle diameter of 110 nm, 4.6 copies of fur nest blacks Polyimide precursor solution 57.0-copy N-methyl pyrrolidone 120.0 copies The light filter was obtained like the glass bead 180.0-copy working example 1. However, the thickness of the black matrix could be 1.4 micrometers. The light sheilding of the black matrix had strong wavelength dependency, and the light

shielding fell by the long wavelength side. Light shieldings were 1.5-2.2 (optical density / $\mu\text{m}$ ), and a rejection in the wavelength of 430-640 nm. The reference-stimuli value Y in the wavelength of 400-700 nm at this time was 0.3.

[0091]The existence of the existence of the pH value of the carbon black used for Table 1-1 by each working example and a comparative example, primary [ an average of ] particle diameter, secondary [ an average of ] particle diameter, and a complementary color pigment, the viscosity of the obtained black paste, a yield value, the light shielding per thickness of a black matrix, and the wavelength dependency of a light shielding was summarized.

[0092]The carboxyl group concentration [COOH] of the surface of the carbon black used for Table 1-2 by each working example and a comparative example, surface hydroxyl group concentration [OH], the sulfone group concentration [SO<sub>3</sub>H] of the surface, primary [ an average of ] particle diameter, secondary [ an average of ] particle diameter, and the existence of a complementary color pigment, The existence of the viscosity of the obtained black paste, a yield value, the light shielding per thickness of a black matrix, and the wavelength dependency of a light shielding was summarized.

[0093]The chromaticity coordinate of the transmitted light of each resin black matrix in illuminant C was summarized in Table 2.

[0094]The chromaticity coordinate of the transmitted light of each resin black matrix at the time of a back light exposure was summarized in Table 3.

[0095]The light transmission of each resin black matrix in each dominant wavelength of a back light was summarized in Table 4.

[0096]The chromaticity coordinate of the transmitted light of each black paste in illuminant C was summarized in Table 5.

[0097]

[Table 1]

表 1 - 1

	カーボンブラック			補色顔料	黒ペースト		ブラックマトリックス	
	P H 値	平均1次粒径 (nm)	平均2次粒径 (nm)		粘度 (cP)	降伏値 (Pa)	膜厚当たりの遮光性 (OD/ $\mu\text{m}$ )	波長依存性
実施例 1	2.8	28	55	青	30	$2.0 \times 10^{-4}$	2.5~2.8	ほとんどなし
実施例 2	3.5	32	60	青+紫	33	$1.0 \times 10^{-4}$	3.1~3.4	ほとんどなし
実施例 3	6.0	26	55	青+紫	25	$4.7 \times 10^{-4}$	3.5~3.8	ほとんどなし
実施例 4	6.0	26	55	青+紫	25	$4.7 \times 10^{-4}$	3.5~3.8	ほとんどなし
比較例 1	8.0	30	80	青	55	$2.5 \times 10^{-1}$	1.9~2.3	あり
比較例 2	8.0	30	80	なし	55	$2.0 \times 10^{-1}$	1.5~2.2	あり

[Table 2]

表 1-2

	カーボンブラック					補色顔料	黒ペースト		ブラックマトリックス	
	[C <sub>OOH</sub> ]	[OH]	[S <sub>O&lt;sub&gt;3&lt;/sub&gt;H</sub> ]	平均1次粒径 (nm)	平均2次粒径 (nm)		粘度 (cP)	降伏値 (Pa)	膜厚当たりの 透光性(OD/μm)	波長依存性
実施例 5	0.004	≤0.001	≤0.001	26	57	青	32	1.0×10 <sup>-4</sup>	2.5~2.8	ほとんどなし
実施例 6	≤0.001	0.005	≤0.001	30	60	青+紫	25	5.0×10 <sup>-5</sup>	3.1~3.4	ほとんどなし
実施例 7	≤0.001	≤0.001	0.005	25	55	青+紫	27	7.0×10 <sup>-4</sup>	3.1~3.4	ほとんどなし
比較例 3	≤0.001	≤0.001	≤0.001	55	110	青	60	3.0×10 <sup>-1</sup>	1.9~2.3	ほとんどなし
比較例 4	≤0.001	≤0.001	≤0.001	55	110	なし	55	2.0×10 <sup>-1</sup>	1.5~2.2	あり

[C<sub>OOH</sub>], [OH], [S<sub>O<sub>3</sub>H</sub>]は全炭素原子当たりのモル比

[Table 3]

表 2

	C光源		ブラックマトリックス		(x <sub>o</sub> -x) <sup>2</sup> +(y <sub>o</sub> -y) <sup>2</sup>
	x <sub>o</sub>	y <sub>o</sub>	x	y	
実施例 1	0.31	0.32	0.32	0.37	0.003
実施例 2	0.31	0.32	0.30	0.31	0.000
実施例 3	0.31	0.32	0.30	0.31	0.000
実施例 4	0.31	0.32	0.29	0.30	0.001
実施例 5	0.31	0.32	0.32	0.37	0.003
実施例 6	0.31	0.32	0.30	0.31	0.000
実施例 7	0.31	0.32	0.30	0.31	0.000
比較例 2	0.31	0.32	0.50	0.42	0.046
比較例 4	0.31	0.32	0.50	0.42	0.046

[Table 4]

表 3

	バックライト光源		ブラックマトリックス		(x <sub>o</sub> -x) <sup>2</sup> +(y <sub>o</sub> -y) <sup>2</sup>
	x <sub>o</sub>	y <sub>o</sub>	x	y	
実施例 1	0.34	0.37	0.35	0.42	0.003
実施例 2	0.34	0.37	0.36	0.36	0.001
実施例 3	0.34	0.37	0.36	0.36	0.001
実施例 4	0.34	0.37	0.37	0.37	0.001
実施例 5	0.34	0.37	0.35	0.42	0.003
実施例 6	0.34	0.37	0.36	0.36	0.001
実施例 7	0.34	0.37	0.36	0.36	0.001
比較例 2	0.34	0.37	0.49	0.44	0.027
比較例 4	0.34	0.37	0.49	0.44	0.027

[Table 5]

表 4

	バックライト主波長での透過率(%)			透過率の比 (最大/最小)
	440~460nm	530~560nm	600~620nm	
実施例 1	0.25	0.44	0.23	1.9
実施例 2	0.32	0.32	0.38	1.2
実施例 3	0.32	0.38	0.38	1.2
実施例 4	0.025	0.025	0.033	1.3
実施例 5	0.25	0.44	0.23	1.9
実施例 6	0.32	0.32	0.38	1.2
実施例 7	0.32	0.38	0.38	1.2
比較例 2	0.05	0.30	0.50	10
比較例 4	0.05	0.30	0.50	10

[Table 6]

表 5

	C 光源		黒色ペースト			$(x_0 - x)^2$ + $(y_0 - y)^2$
	$x_0$	$y_0$	Y	x	y	
実施例 1	0.31	0.32	0.28	0.32	0.37	0.003
実施例 2	0.31	0.32	0.25	0.31	0.31	0.000
実施例 3	0.31	0.32	0.22	0.30	0.31	0.000
実施例 5	0.31	0.32	0.28	0.32	0.37	0.003
実施例 6	0.31	0.32	0.25	0.31	0.31	0.000
実施例 7	0.31	0.32	0.22	0.30	0.31	0.000
比較例 2	0.31	0.32	0.30	0.50	0.42	0.046
比較例 4	0.31	0.32	0.30	0.50	0.42	0.046

Thus, the chromium black matrix of a liquid crystal display element (TFT (thin film transistor) type) and others which carries the light filter which has the manufactured resin black matrix, It is a contrast ratio (the ease of being visible: although it generally defines as white luminosity / black luminosity) of CRT (color Braun tube) as the liquid crystal display element and comparison which have a two-layer chromium black matrix. When there was a reflected light, the indoor illumination dependency expressed with (white luminosity + reflective)/(black luminosity + reflection) was compared (drawing 1). Luminosity was measured by the TOPCON black matrix 5 or the black matrix 7. When indoor illumination was high, there were few falls of the contrast ratio of the liquid crystal display element in which the light filter which has a resin black matrix was carried, and the result said that the display is legible also at a bright place was obtained. The tint of (4) reflections with a small reflect lump of (3) backgrounds with (2) black appropriate for [ backgrounds ] black to which (1) red and green and blue coloring look skillfully as for the feature of the liquid crystal display element of resin-black-matrix light filter loading perceived sensuously had dropped off.

[0098]When 100 monitor investigations were conducted, the data which supports the feature of



the liquid crystal display element of resin-black-matrix light filter loading statistically was obtained.

[0099]The light filter of this invention could obtain the light filter for liquid crystal display elements which has the black matrix which was excellent in the color characteristic by distributing a shielding agent specific in resin as mentioned above, and the liquid crystal display element which was excellent in display quality was obtained.

[0100]

[Effect of the Invention]The resin black matrix of this invention can improve dispersibility by distributing carbon black specific as a shielding agent in resin as mentioned above, The black matrix which is high, and is excellent in pattern processing nature, and does not have film peeling etc. can be acquired, and the liquid crystal display element which was excellent in display quality is obtained. [ of a light sheilding ] The outstanding resin black matrix is acquired by applying the black paste obtained by distributing specific carbon black in a resin solution.

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[Translation done.]